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(54) Title: LOW EMISSIONS DIESEL FUEL

(57) Abstract

A low emission diesel fuel suitable for use in underground diesel-engined mining equipment comprises a straight run distillate fuel having an end point not greater than 300 °C (about 660 °F), a cetane number in the range of 55 to 60, a specific gravity not greater than 0.83, a sulfur content not greater than 0.1 wt. percent and an aromatics content of 18 to 30 wt. percent. The T_{90} of the fuels is typically in the range of 255° to 270 °C (about 490 °F to 525 °F), with an initial boiling point typically in the range of 170° to 190 °C (about 340° to 374 °F). Ten percent points (T_{10}) are typically in the range from about 200° to 220 °C (about 390° to 430 °F). The API gravity of the fuel is at least 38 and is typically in the range of 38 to 42 and the specific gravity is typically in the range of 0.82 to 0.83.

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LOW EMISSIONS DIESEL FUEL

This invention relates to diesel fuels and more particularly to diesel fuels which produce lower levels of vehicle emissions and which are suitable for use in underground mining engines.

A number of performance specifications have been established for diesel fuels of different grades depending upon service application. A number of different properties are set out in these specifications including, for example, flash point, cloud point, pour point, viscosity, sulfur content, distillation range, gravity and ignition quality. Of these, the ignition quality is an important parameter and is usually expressed in cetane number (CN) determined by the standard ASTM test method D613. Diesel fuels of high cetane number differ from those of lower cetane numbers by having shorter ignition lags when the fuel is injected into the cylinders of the engine. Fuels of high-cetane number also ignite at lower compressed air temperatures than the lower-cetane fuels, permitting the engine to be started at lower temperatures and to be brought to a steady running condition more quickly with less combustion knock.

Viscosity is another important characteristic of diesel fuels, affecting leakage in the fuel pump and the power required to operate the pump as well as having an influence on the size of the fuel droplets sprayed into the cylinder through the injection nozzles. Viscosity is typically expressed as kinematic viscosity, determined by ASTM test D445.

Current environmental regulations are setting stricter specifications on diesel fuels, especially in terms of sulfur content and aromatics level. Sulfur is, of course, associated with the production

of acidic oxides of sulfur, a troublesome atmospheric pollutant. Aromatics are considered undesirable not only for their adverse effect on ignition quality but also because they have been implicated with the production of significant amounts of particulates in the engine exhaust.

One type of service where increasing government regulation is being proposed is in underground mines where a concern for improved air quality standards has been expressed. Although improved engine design and maintenance, increased air circulation or a reduced level of engine operations in the mines could improve air quality, each of these presents its own problems. Another solution lies in the use of fuels which result in lower levels of harmful emissions.

The present invention provides a diesel fuel which produces low levels of engine emissions and which can be readily produced in existing refineries by proper observance of product specifications coupled with suitable additive use. The present diesel fuel compositions are especially suitable for use in underground diesel-engined mining equipment and are capable of reducing all of the currently regulated emissions subject to government regulation, namely, carbon monoxide, oxides of nitrogen, unburned hydrocarbons and particulates. The properties of the present low emission fuels are low sulfur content, low final boiling range and a high but controlled emission quality.

According to the present invention diesel fuels comprise a straight run distillate fuel having an end point not greater than 300°C (572°F), a cetane number in the range of 55 to 60 a specific gravity not greater than 0.83, a sulfur content not greater than 0.1 wt% and an aromatics content of 18 to 25%. These

fuels are also distinguished by a number of other product characteristics which are discussed below.

In the accompanying drawings figures 1 and 2 are graphs which show the results of particulate emissions testing for a low emission diesel fuel and a conventional autodiesel fuel.

The key feature of the present diesel fuels is the high but controlled emission quality of these fuels. The cetane number is maintained in the range of 55 to 60, preferably 55 to 58. Higher cetane numbers are considered undesirable because we have found that although gaseous emissions decrease as the cetane number increases the particulates increase. Maintaining the emission quality in the specified range therefore enables both types of emissions to be maintained at minimum values. The cetane index (ASTM D976-80) is typically in the range of 46 to 52. The cetane number of the base fuel may be improved by the use of cetane number improvers such as the alkyl nitrates e.g. octyl nitrates.

The distillation of the fuel is controlled so as to limit the density of the fuel since high densities have been found to contribute significantly to the emission of particulates. When the density is controlled in an appropriate manner, the aromatics content may extend up to about 30 weight percent or more; it has been found that the aromatics present in the controlled density, low emission fuels, mainly alkyl benzenes, naphthene benzenes and naphthalenes, are not harmful, either in terms of their effects on combustion quality or on engine emissions. The final boiling point of the fuels is therefore held below about 315°C (600°F) and preferably below 300°C (572°F). Provided that this limitation is observed, bicyclic and polycyclic aromatics will be

substantially excluded. The T_{90} (90% boiling point) of the fuels is typically in the range of 255° to 270°C (490°F to 525°F).

The initial boiling points of the fuels is lower than conventional, typically in the range of 170° to 190°C (340° to 374°F). Ten percent points (T_{10}) are typically in the range from 200° to 220°C (390° to 430°F). The use of the lower initial points ensures that a significant amount of paraffins is present which contributes to the high cetane numbers characteristic of the present fuels. They also contribute to the characteristic high API gravity (ASTM D1298-3) of the fuels which is at least 38 and is typically in the range of 38 to 42, usually about 40. This contrasts with the lower API gravities of conventional fuels, normally in the range of 30 to 37. The specific gravity of the present fuels (ASTM D 4052-9) is, consistent with the low boiling range, lower than that of conventional fuels, typically in the range of 0.82 to 0.83, contrasting with values of about 0.84 to 0.88 for conventional fuels. Also consistent with the presence of the lower boiling materials in the fuels is a relatively low viscosity, typically from 1.7 to 1.9 mm^2/s at 40°C (ASTM D445-3) and from about 2.4 to 2.8 at 20°C (ASTM D445-9). Again, this is in contrast to the higher viscosity characteristics of conventional automotive diesel fuels, which are typically about 3 to 4 mm^2/s at 40°C. It has been found, however, that the present fuels may be used in conventional injection pumps without increasing leakage or other harmful effects.

In order to reduce the level of sulfate particulates in the engine exhaust, the sulfur is held to a maximum of 0.1 wt percent and preferably below 0.05 wt percent. The use of suitable crude

sources or refinery hydrotreatment, sulfur levels of 0.01 wt. percent may be attained and are desirable from the emissions standpoint. Nitrogen, by contrast, is not especially low, typically no more than 150 ppmw.

The distillate fuels are straight run i.e not cracked, distillate stocks and this characteristic is reflected in their olefin content which is below 10 wt. percent and usually below 8 wt. percent. Saturates, by contrast, make up about 65 to 70 wt. percent of the fuel with aromatics being no more than about 35 wt. percent, usually in the range of 24 to 30 wt. percent.

Other product specifications are generally characteristic of diesel fuels for use in high speed engines, with flash point, pour point and cloud point being according to established specifications. Typically, the flash point of the present fuels is in the range of 55° to 65°C (130° to 150°F) which is in compliance with established specifications. Pour points are typically below -30°C (below -20°F) and cloud points lower than -25°C (-15°F).

An additive package is incorporated into the present fuels, comprising a detergent, a friction reducer and a cetane improver. Conventional materials may be used for this purpose. The detergent maintains cleanliness in the injectors and other close-tolerant components especially those close to the higher temperature areas of the engine. The friction reducer maintains long injection pump life and also assists operation of the injectors by facilitating opening of injection nozzle pintles and atomization of the fuel in the nozzle region. The cetane improver is used in its conventional role of improving combustion quality.

A number of conventional additives of these types may be used. We have found a particularly preferred combination is to use a succinimide type detergent, preferably a poly (alkenyl) succinimide. A suitable treat rate for detergents of this kind to impart the desired detergency properties is from 60 to 80 pounds per thousand barrels (ptb), preferably 75 ptb, although the treat rate used should be selected according to the characteristics of the detergent in actual use. A preferred detergent is a polybutenyl bis(succinimde) produced from a polybutenyl succcinic anhydride and tetraethylene pentamine (2:1 ratio, pb mol. wt. about 1200) in combination with ethylene diamine tetraacetic acid. This combination is described in U.S. Patent No. 4,971,598.

A suitable friction reducer is typically used at a treat rate which is sufficent to confer the desired reduction in friction, typically from about 5 to 10 ptb, preferably about 7 ptb. A suitable friction reducer comprises a dimer acid having 36 carbon atoms (acid dimer of oleic acid) in combination with nonylphenol. A suitable commercial friction reducer is the one sold under the trademark Mobiladd F-800.

Conventional cetane number improvers such as the alkyl nitrates e.g. octyl nitrate, may be used in amounts appropriate to the desired ignition quality, typically from 0.1 to 0.5 volume percent, preferably about 1 to 2, e.g. about 1.5, volume percent.

Other additives of the kinds normally used in diesel fuels may also be present in conventional amounts to impart the desired properties to the fuel, for example, antistatic additives, antioxidants and stabilizers to improve storage stability, dyes for color etc.

The present fuels may be prepared by conventional refinery processing of suitable crudes. Being straight run products, the fuels may be produced directly by suitable fractionation after removal of contaminants in the desalter. Hydrotreating may be used if desired to reduce the sulfur level.

Product Testing

Two low emissions diesel fuels (LEDF) were prepared in two separate refineries by distillation from a paraffinic crude source (Bass Strait, Australia) and an additive package comprising a polyisobutylene succinimide detergent (treat rate 0.21 g/l or 75 pounds per thousand barrels) a friction reducer (0.02 g/l or 7 pounds per thousand barrels) and a cetane improver (octyl nitrate) at a rate of 1 volume percent was added. The properties of the two fuels are shown in Table 1 below.

Table 1
Fuel Properties

	LEDF - 1	LEDF - 2
API Gravity	40.6	40.4
Density @ 15C	0.8226	0.8239
Viscosity, cs. @ 20°C	2.5	2.8
Viscosity, cs. @ 40°C	1.7	1.9
Flash Point, °C (°F)	58(137)	61(141)
Pour Point, °C (°F)	-37(-35)	-32(-25)
Cloud Point, °C(°F)	-36(-32)	-28(-18)
Nitrogen, ppm	130	130
Sulfur %	0.01	0.06
Aromatics, %, FIA-D1319-1	24	24
Dilstillation Temperature, °C(°F)		
IBP	177(350)	181(357)
T10	205(401)	214(418)
T50	232(450)	241(465)
T90	259(498)	266(510)
EP	282(540)	299(571)
Cetane Number	56.4	59.0
Cetane Index, D 976-80	47.8	50.0

The two fuels were tested for emissions in three different engines, a Cummins 6BT engine, a GM 6.5 liter engine with turbocharger and intercooler and a Mercedes Benz OM366LA 6 cylinder, turbocharged and intercooled engine. The Cummins and GM engines were run on the U.S. Federal Test procedure (FTP) emission cycle while the MB engine was run of the ECE R-49 test cycle used to certify heavy duty engines in Europe. The percentage improvement in emissions is shown in Table 2 below, with the improvements reported as relative to those obtained with average results from two conventional, commercial automotive diesel fuels.

Table 2
Improvement in Emissions

	LEDF-1				LEDF-2			
	HC	CO	NOx	Part	HC	CO	NOx	Part.
Cummins 6BT								
FTP Cycle	34	17	12	65	31	23	16	56
Steady State								
Idle	15	14	12	19	26	25	11	28
30 mph	8	4	1	54	14	11	5	54
50 mph	0	-1	3	20	11	9	6	25
GM 6.5 Liter								
FTP Cycle	31*	16	7	28	-8*	36	7	-2
MB OM366LA								
ECE R-49	13	20	3	13	17	28	4	18
Average (2)	24	18	7	35	24	29	9	24
Overall Average(2)	24	24	8	29				

(1) Improvements compared to average results from two conventional auto diesel fuels
(2) Average FTP and ECE R-49

* Not included in average

As shown above, the low emission diesel fuel reduced emissions in all three test engines, using the two different test cycles. The average emissions reductions were 16 to 30% in hydrocarbons, 9 to 33% in carbon monoxide, 4 to 12% in NOx and 26 to 32% in particulates. These emissions reductions represent a significant benefit for the low emission fuels which of particular utility in underground mining environment.

Particulate Emissions

The large reduction in particulate emissions with the Cummins engine were confirmed by analysis of the particulate emissions from LEDF-1 above. The soluble organic fraction (SOF) of the particulates was extracted from the filter paper using a methylene chloride solvent. The SOF, the fuel itself and the lubricant used in the engine (Mobil 1 synthetic oil) were subjected to gas chromatography. The test methodology used for analyzing the soluble organic fraction of the particulate is described in SAE paper 870626 "Direct analysis of diesel particulate-bound hydrocarbons by gas chromatography with solid sample injection". The results are shown in Figures 1 and 2 of the drawings. Figure 1 shows the curves with the low emission diesel fuel (LEDF-1) and Figure 2 the results obtained with a conventional automotive diesel fuel. In both cases, the upper curve gives the GC analysis for the SOF, the middle curve the GC analysis for the fuel itself and the bottom curve the GC analysis for the lubricant.

The conventional automotive diesel fuel gives an SOF trace showing components from both the fuel and from the lube indicating that significant hydrocarbon emissions are caused by the use of this fuel. By contrast, the GC trace from the LEDF is

almost entirely free of the fuel components, indicating a significant reduction in hydrocarbon emissions.

Claims:

1. A low emission diesel fuel having a cetane number in the range of 50 to 60, which comprises:
(i) a straight run hydrocarbon distillate having an initial boiling point in the range of 170° to 190°C, an end point not higher than 315°C, a sulfur content of less than 0.1 wt percent and aromatics content of 18 to 30 wt. percent, a maximum specific gravity of 0.83 at 15°C and an API gravity of 38 to 43, and
(ii) an additive package comprising a detergent, a friction reducing additive and a cetane number improver.

2. A diesel fuel according to claim 1 in which the initial boiling point of the distillate is in the range of 170 to 180°C.

3. A diesel fuel according to claim 1 in which the 10 percent point of the distillate is from 200° to 220°C.

4. A diesel fuel according to claim 1 in which the end point of the distillate is not greater than 300°C.

5. A fuel according to claim 1 in which the 90% point of the fuel is in the range of 255° to 270°C.

6. A fuel according to claim 1 in which the API gravity of the distillate is from 39 to 42.

7. A diesel fuel according to claim 1 in which the specific gravity of the fuel at 15°C is from 0.82 to 0.83.

8. A diesel fuel according to claim 1 in which the maximum sulfur content is from 0.005 to 0.05 wt%.

9. A diesel fuel according to claim 1 which has a cetane number in the range of 55 to 60.

10. A diesel fuel according to claim 9 which has a cetane number in range of 55 to 58.

11. A diesel fuel according to claim 1 in which the detergent of the additive package comprises a polyalkenyl succinimide detergent.

12. A diesel fuel according to claim 11 in which the polyalkenyl succinimide detergent comprises a polyisobutenyl succinimide.

13. A diesel fuel according to claim 1 in which the friction reducer comprises dimer acid.

14. A diesel fuel according to claim 1 in which the cetane improver comprises an alkyl nitrate.

15. A diesel fuel according to claim 1 in which the cetane improver comprises octyl nitrate.

16. A diesel fuel according to claim 1 in which the detergent is present in the amount of 0.17 to 0.23 g/l of the finished fuel.

17. A diesel fuel according to claim 1 in which the friction reducer is present in the amount of 0.014 to 0.028 g/l of the finished fuel.

18. A diesel fuel according to claim 1 having a pour point below -30°C.

19. A diesel fuel according to claim 1 having a cloud point below -25°C.

20. A diesel fuel according to claim 1 having a flash point in the range of 55 to 65°C.

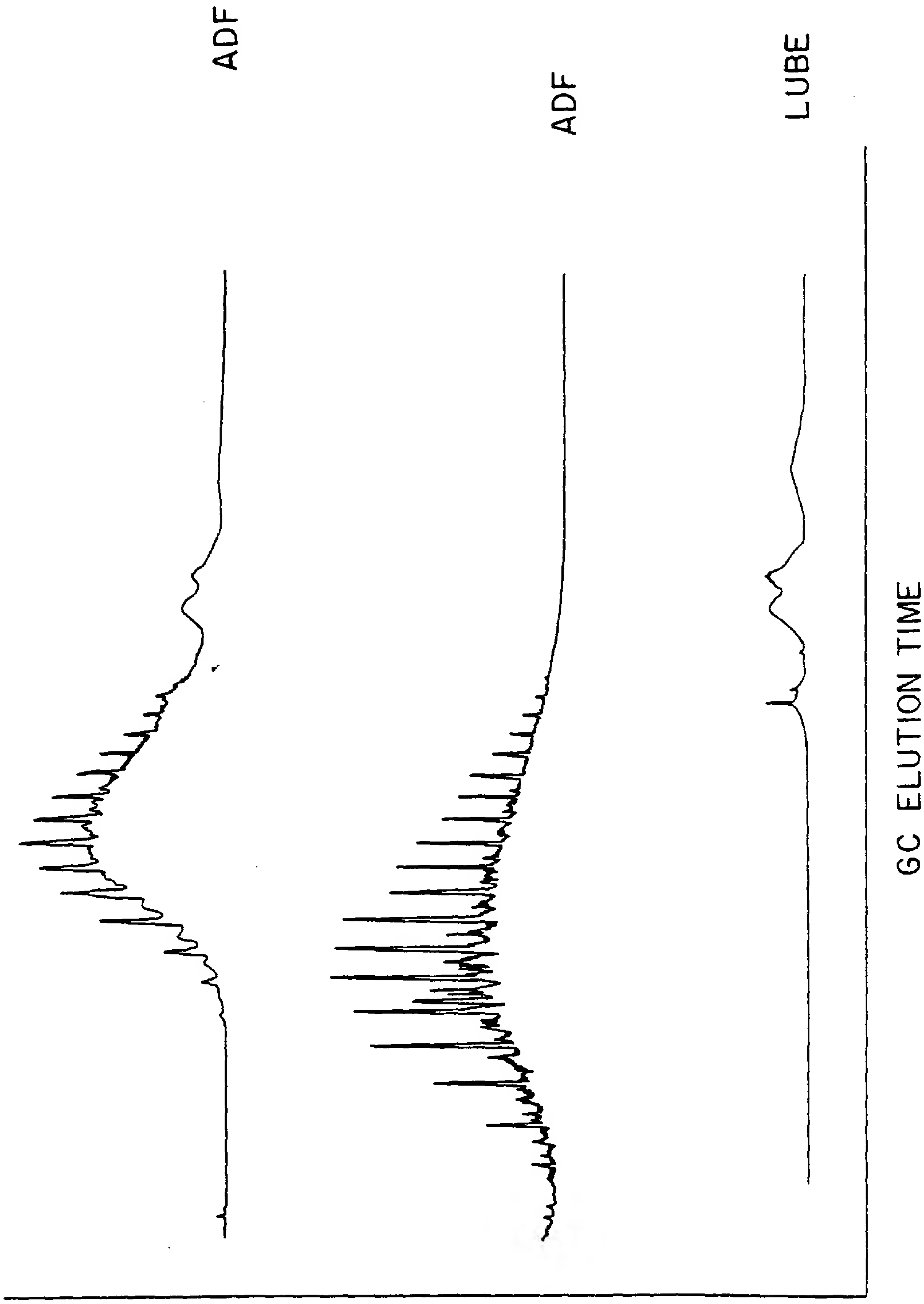

FIG. I

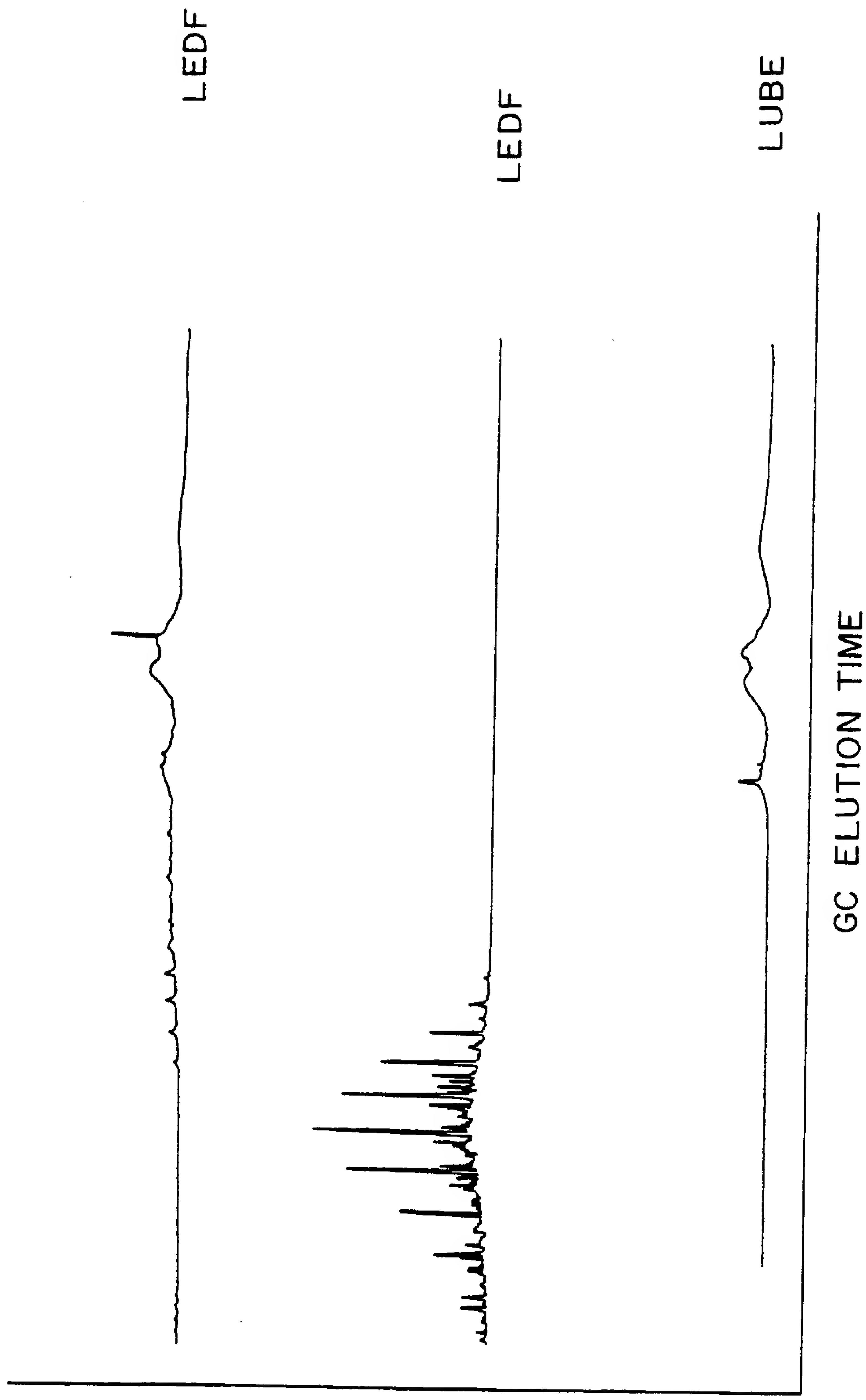

FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/02254

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C10L 1/22
US CL :44/413, 418, 457
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 44/413, 418, 457

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Kirk-Othmer, "Encyclopedia of Chemical Technology" (John-Wiley), Volumes 11, 17 (1980).

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Chevron Research and Development Company Publication No. 930728, March 1993, Manuch Nikanjam, "Development of the First CARB Certified California Alternative Diesel Fuel", pages 1-14	1-20
Y	Kirk-Othrmer, "Encyclopedia of Chemical Technology", Volume 11, published 1980, John Wiley & Sons (New York), pages 682 to 689	1-20
Y	Kirk-Othmer, "Encyclopedia of Chenical Technology", volume 17, published 1982, John Wiley & Sons (New York), page 268	1-20
Y	US, A, 4,482,356 (Hanlon) 13 November 1984, all pages	1-20

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
03 MAY 1994	24 MAY 1994

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